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**MAGNETIC PROPERTIES AND SITE  
DISTRIBUTIONS IN THE SYSTEM  $\text{FeCr}_2\text{O}_4\text{-Fe}_3\text{O}_4$ ,  
( $\text{Fe}_2\text{+ Cr}_{2-x}\text{Fe}_{3+x}\text{O}_4$ )**

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MAGNETIC PROPERTIES AND SITE DISTRIBUTIONS  
IN THE SYSTEM  $\text{FeCr}_2\text{O}_4\text{-Fe}_3\text{O}_4$ ,  $(\text{Fe}^{2+}\text{Cr}_{2-x}\text{Fe}_x^{3+}\text{O}_4)$

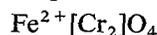
by M. ROBBINS, G. K. WERTHEIM, R. C. SHERWOOD and D. N. E. BUCHANAN  
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**Résumé.** — Le système  $\text{Fe}^{2+}\text{Cr}_{2-x}\text{Fe}_x^{3+}\text{O}_4$  est caractérisé à l'aide de mesures magnétiques et de l'effet Mössbauer. Nous obtenons des renseignements sur la transition en faisant varier  $x$  pour passer du spinelle normal  $\text{FeCr}_2\text{O}_4$ , matériau ferromagnétique à spin incliné, au spinelle inverse  $\text{Fe}_3\text{O}_4$ , matériau ferrimagnétique avec des spins colinéaires.

**Abstract.** — Magnetic and Mössbauer effect measurements have been used to characterize the system  $\text{Fe}^{2+}\text{Cr}_{2-x}\text{Fe}_x^{3+}\text{O}_4$ .

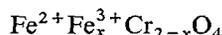
We obtain information on the transition with increasing  $x$  between the normal spinel  $\text{FeCr}_2\text{O}_4$ , which has a canted-spin structure, and the inverse spinel  $\text{Fe}_3\text{O}_4$ , a ferrimagnet with collinear spins.

The spinel system  $\text{FeCr}_2\text{O}_4\text{-Fe}_3\text{O}_4$  was studied crystallographically between room temperature and  $\sim 80^\circ\text{K}$  by Francombe [1]. Interest in this system arises from the fact that  $\text{FeCr}_2\text{O}_4$  is a canted spin antiferromagnet [2] while  $\text{Fe}_3\text{O}_4$  is a Néel antiferromagnet with collinear spins. Further more,



is a normal spinel while magnetite,  $\text{Fe}^{3+}[\text{Fe}^{2+}\text{Fe}^{3+}]\text{O}_4$ , is an inverse spinel. The effects of site substitution on the B-site charge hopping conductivity of magnetite and the metal-insulator transition at  $119^\circ\text{K}$  are also of interest.

The preparation of materials in the system



has been described elsewhere [4]. Room temperature unit cell parameters obtained by x-ray diffraction are shown in figure 1, and are in reasonable agreement with those reported by Francombe [1]. This system can be divided into three regions: 1)  $0 \leq x \leq 0.68$ , 2)  $0.75 \leq x \leq 1.38$ , 3)  $1.50 \leq x \leq 2.0$ .

Mössbauer measurements of samples in region 1 show that  $\text{Fe}^{3+}$  occupies the octahedral B-sites and  $\text{Fe}^{2+}$  the tetrahedral A-sites exclusively. The substitution of iron for chromium results in the appearance of two well-resolved quadrupole-split spectra. One has an isomer shift (IS) characteristic of A-site  $\text{Fe}^{2+}$  and a quadrupole splitting (QS) which increases with iron substitution. The other has an IS very close to that of  $\text{ZnFe}_2\text{O}_4$  [5]. It also has a small, largely temperature and composition independent QS, characteristic of  $\text{Fe}^{3+}$  in a noncubic site, i. e.  $\text{Fe}^{3+}$  in the B-site with  $\bar{3}$  m symmetry. Since the recoil-free fractions of the A- and B-sites in the spinels are known to be similar [6], the absorption areas provide a good measure of the site occupancy. The measured ratios of  $\text{Fe}^{3+}/\text{Fe}_{\text{total}}$  are in accord with the nominal compositions provided the iron substituted for chromium all enters the B-site as  $\text{Fe}^{3+}$ . The data give no indication of charge hopping between  $\text{Fe}^{2+}$  on the A-sites and  $\text{Fe}^{3+}$  on the B-sites.

The Curie temperature ( $T_c$ ) increases linearly for  $x \leq 0.5$ , and more rapidly for  $0.5 < x \leq 0.68$ . The magnetic moment of  $0.8 \mu_B$  for  $\text{FeCr}_2\text{O}_4$  is also in qualitative agreement with previously reported values [1], which have been ascribed [7] to canting of the

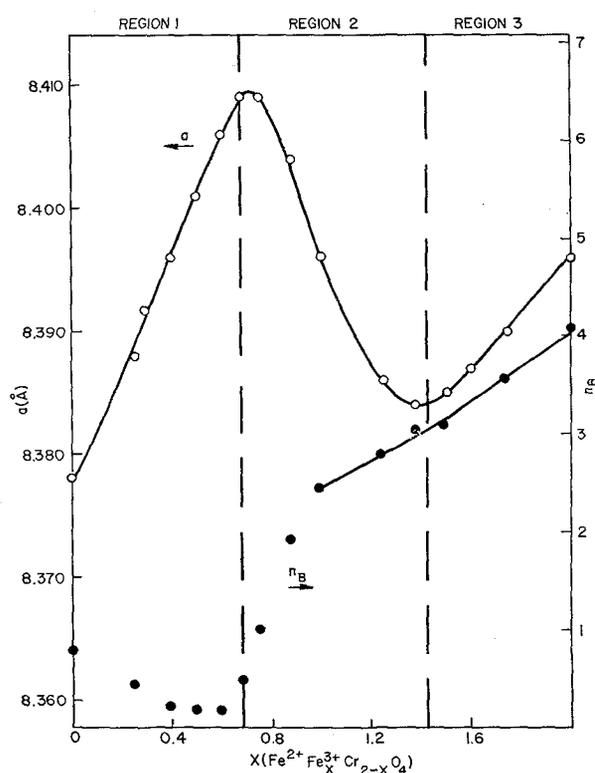


FIG. 1. — Room temperature unit cell parameters,  $a$ , and magnetic moment,  $n_B$  ( $H = \infty$ ,  $1.5^\circ\text{K}$ ), vs composition,  $x$ .

B-site moment. The substitution of  $\text{Fe}^{3+}$  with  $5 \mu_B$  on the B-site serves to increase the B-site moment and consequently cause an initial decrease in the net moment. The occurrence of the minimum between  $x = 0.5$  and  $0.6$  figure 1, suggests that the canting angles of the B-site ions with  $\text{Fe}^{3+}$  substitutions are not as great as that of  $\text{Cr}^{3+}$  in  $\text{FeCr}_2\text{O}_4$ .

In Region 2 room temperature unit cell parameters decrease with increasing  $x$ . Mössbauer effect data show that divalent iron is being displaced to the B-site. Two important conclusions can be drawn: (1) the boundary between Regions 1 and 2 corresponds to the beginning of the displacement of  $\text{Fe}^{2+}$  by  $\text{Fe}^{3+}$  on the A-site, enhancing the A-B exchange, and (2) charge hopping begins as soon as  $\text{Fe}^{2+}$  is displaced

to the B-site. These factors help bring about a collinear spin arrangement for iron moments on the B-sites, which is consistent with the rapid increase in moments.

In Region 3 room temperature Mössbauer data show two six-line hfs absorption patterns, similar to those of magnetite [8]. The pattern corresponding to A-site  $\text{Fe}^{3+}$  changes very little with the substitution of  $\text{Cr}^{3+}$  on the B-site. The other, corresponding to the total B-site iron has an isomer shift indicative of an average valence of  $2.5^+$ . The line broadening shows that the hopping is not fast enough to restore the natural linewidth.

The Mössbauer absorption areas and isomer shifts indicate a pronounced tendency to retain equal amounts of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  on the B-site. Although the possibility remains that more  $\text{Fe}^{3+}$  than  $\text{Fe}^{2+}$  is displaced from the B-site, the alternative that  $\text{Cr}^{3+}$  replaces only  $\text{Fe}^{3+}$  from the B-site can be conclusively ruled out. This tendency to retain equal amounts of the two valences on the B-sites is undoubtedly related to the pairwise charge hopping which has been found in nonstoichiometric magnetite [9]. It should also tend to stabilize  $\text{Fe}^{2+}$ - $\text{Fe}^{3+}$  pairs in substituted material.

Curie temperatures and magnetic moments increase linearly with increasing  $\text{Fe}^{3+}$  substitution. The moment found for  $\text{Fe}_3\text{O}_4$  is in agreement with published values [10]; but the others are lower than those calculated using collinear spins. High  $T_c$  in this region indicate strong A-B interactions. This and the presence of charge hopping of Fe on the B-sites make it reasonable to assume collinear spins for all of the iron ions. The low observed moments may therefore be explained by assuming that the  $\text{Cr}^{3+}$  moments on the B-sites are canted in all of the materials studied.

Using the results of Mössbauer and magnetic measurements, it is possible to construct the diagram in figure 2, which summarizes the site distribution as a function of composition. In Region 1 all added  $\text{Fe}^{3+}$  goes into the B-site. In Region 3 added  $\text{Cr}^{3+}$  displaces equal amounts of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  from the

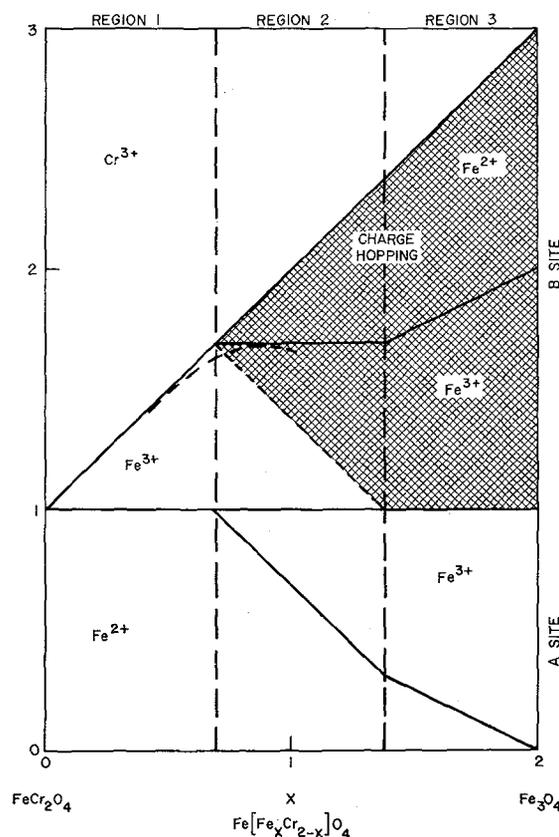


FIG. 2. — Site distribution diagram.

B-site. In Region 2, drawn so as to connect Regions 1 and 3, each added  $\text{Cr}^{3+}$  displaces one  $\text{Fe}^{2+}$  from the B-sites. When  $x < 1$  most of the  $\text{Fe}^{2+}$  is found on the A-sites and charge hopping disappears. The A-B interactions are weakened and the increasing amounts of  $\text{Cr}^{3+}$  on the B-sites increases the strength of the next-nearest neighbor B-B antiferromagnetic interactions which cause canting of the Fe ion moments as well as those of  $\text{Cr}^{3+}$ .

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