JOURNAL OF SOLID STATE CHEMISTRY 79, 189–193 (1989)

Effect of Fe^{3+} Incorporation on the Fe^{2+} Clustering in $FeGa_2O_4$

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Received June 10, 1988; in revised form December 22, 1988

Magnetization and Mössbauer effect studies have been carried out on samples of $Fe_{1+x}Ga_{2-x}O_4$ for x = 0.2, 0.5, 0.6, 0.8, and 1.0. The results show Fe^{2+} ion clusters are present in the samples with $x \leq 0.2$. On increasing x, clustering is removed and Fe^{3+} ions are distributed between the two lattices giving rise to strong A–B interactions.

Introduction

Studies on $FeGa_2O_4$ have shown that Ga^{3+} and Fe^{2+} ions are present in both octahedral (B) and tetrahedral (A) sites of the spinel lattice (*1, 2*) and the distribution of these ions on the two sites depends on the annealing temperature and subsequent heat treatment of the spinel oxide (*1, 3*). Presence of Fe^{2+} ions on both sites allows only a small concentration of the magnetic ions on either site and strong A–A, B–B, or A–B interactions cannot be expected in $FeGa_2O_4$ and consequently the ordering temperature of this spinel is only 11 K. Furthermore, neutron diffraction and Mössbauer spectroscopy studies on this compound by Ghose *et al.* (*1*) have shown that the Fe^{2+} ions are not randomly distributed in each sublattice but form clusters within which short-range magnetic order is present.

Clustering of Fe^{2+} ions can be prevented if the concentration of these ions are increased at the cost of the diamagnetic Ga^{3+} ions. But divalent iron cannot be substituted for trivalent gallium without disturbing the stoichiometry and spinel structure of the ferrite. However, if Fe^{3+} is used instead of Fe^{2+}, the iron concentration can be increased without disturbing the spinel lattice. The present work was thus taken up to study the magnetic properties of Fe^{3+} substituted $FeGa_2O_4$ and determine the Fe^{3+} ion concentration which would completely remove clustering of Fe^{2+} ions in gallium ferrite.

Experimental

Samples of $Fe_{1+x}Ga_{2-x}O_4$ were prepared from Fe_2O_3, Ga_2O_3 (Mathey, 'specpure'), and Fe (E. Merck). Details of the preparation for x = 0, 0.2, 0.5, 0.6, 0.8, and 1.0 have been given elsewhere (*6*). Samples with $x > 1$ were not prepared as the clustering of Fe^{2+} ions were absent in iron-rich samples.

The room temperature X-ray powder patterns were taken in Cu$K\alpha$ radiation using a Siemens K4 diffractometer. Magnetization measurements were made in the range 4–300 K using a vibrating-sample magnetometer equipped with a helium gas-flow cryostat. The Mössbauer spectra were recorded

0022-4596/89 $3.00

using a conventional constant acceleration system with data collection in a 400-channel PHA. The source was 10 mCi/^{57}Co in Rh.

Results and Discussion

X-ray diffraction studies for the compounds in the system $Fe_{1+x}Ga_{2-x}O_4$ show that single-phase cubic spinel compounds are formed in the studied composition range $x = 0$ to $x = 1$. The plot of composition versus lattice parameter in Fig. 1 shows a large negative deviation from Vegard's law as the concentration of iron increases. Such negative deviations are usually found when substitution brings about a change in cation distribution and the same type of ion is present on both sites. In $Fe_{1+x}Ga_{2-x}O_4$, both Ga^{3+} and Fe^{3+} ions have preference for the tetrahedral (*A*) site while Fe^{2+} ions prefer the octahedral (*B*) sites. Hence on substitution of Ga^{3+} ions by Fe^{3+} ions, Fe^{2+} ions are likely to be displaced to the *B* sites and the Fe^{3+} ions can then occupy the *A* sites. Such displacement of ions from one site to another of the spinel lattice has also been found in $Fe^{2+}Cr_{2-x}Fe^{3+}_xO_4$ (*4*) and $CuCr_{2-x}Al_xO_4$ (*5*) spinel systems. However, for $x > 0.6$, the Fe^{3+} ions probably occupy the *B* sites since cation distribution of $FeGa_2O_4$ shows that Fe^{2+}_A is 0.6 (*1*) and, hence, for $x > 0.6$ no vacancy in the *A* sites due to displacement of Fe^{2+}_A will result. The minima in the lattice parameter vs composition curve may thus indicate this change in Fe^{3+} ion occupation from *A* site to *B* site.

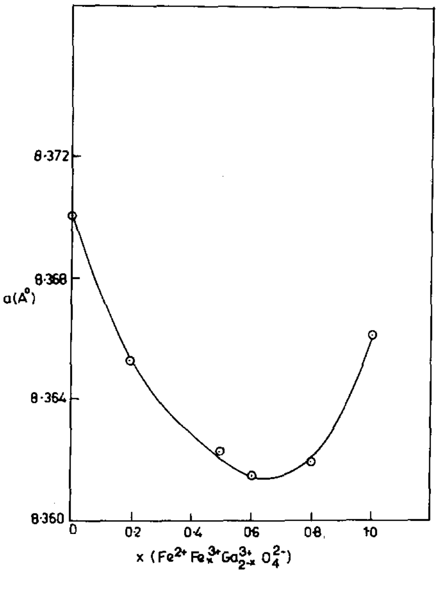

FIG. 1. Room temperature unit cell parameter *a* (Å) vs composition (*x*) for the system $Fe_{1+x}Ga_{2-x}O_4$.

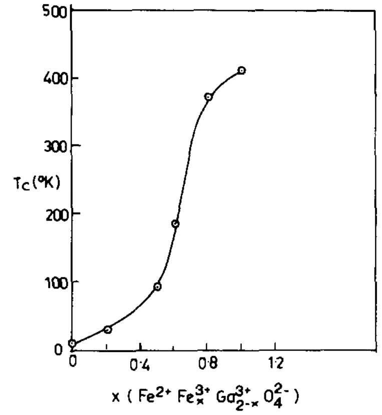

FIG. 2. Curie temperature vs composition.

The displacement of Fe^{2+}_A ions to the *B* sites on introduction of Fe^{3+} ions is also supported by the magnetization studies. The results show the absence of Fe^{2+} ion clustering and also a rise in Curie temperature (T_C) as *x* is increased. With an increase in the concentration of Fe^{2+} ions on the *B* sites the probability of cluster formation is reduced. Absence of clustering would allow all the Fe^{2+}_B ions to take part in long-range magnetic interactions and hence with increasing *x* there should be an increase in the Curie temperature. This is manifest in Fig. 2. However, as *B*–*B* interactions are not very strong, the T_C values of compounds with $x < 0.6$ are not expected to be very high and so the T_C vs composition plot

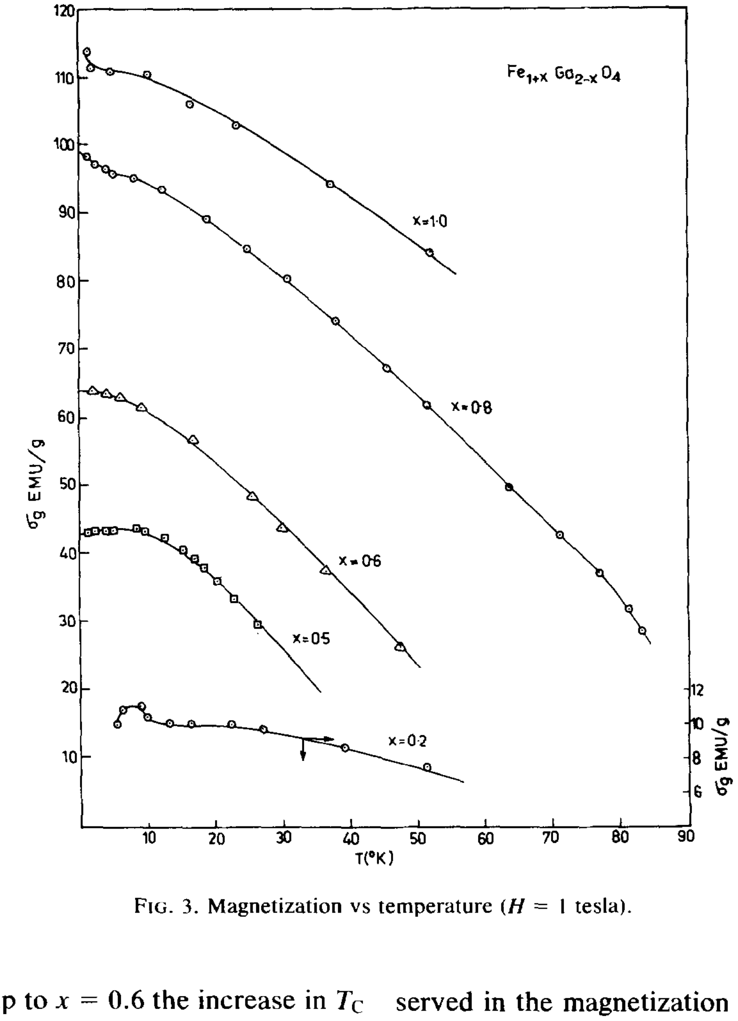

FIG. 3. Magnetization vs temperature (H = 1 tesla).

shows that up to $x = 0.6$ the increase in T_C is gradual. For $x > 0.6$, T_C values rise quite rapidly. High T_C values in spinel oxides imply strong antiferromagnetic interaction between A site and B site cations and this is possible only when the magnetic ions are distributed between the A and B sites of the spinel lattice. As has been discussed above, for $x > 0.6$, the Fe^{3+} ions are present in both A and B sites, and the strong magnetic interactions leading to high T_C values are between Fe_A^{3+} and Fe_B^{3+} ions.

The magnetization versus temperature plots in Fig. 3, show that for $x = 0.2$, there is an additional hump in the curve well below the Curie temperature. Anomaly observed in the magnetization curves of certain spinels has been attributed to either a change from collinear to canted spins or to clustering of ions. In $MnCr_2O_4$ and CoV_2O_4, it was attributed to canting of spins (*6*), while in some of the $Fe_{1+x}Cr_{2-x}O_4$ (*4*) spinels and in $FeGa_2O_4$ (*1*), it was thought that the anomaly is due to clustering of ions. In $FeGa_2O_4$ the clustering of ions giving rise to short-range magnetic order has been well established from Mössbauer and neutron diffraction studies. In $Fe_{1.2}Ga_{1.8}O_4$ also clustering of Fe^{2+} ions has been suggested from Mössbauer studies (*7*). The Mössbauer spectra of $Fe_{1.2}Ga_{1.8}O_4$ showed a hyperfine split pattern indicating the pres-

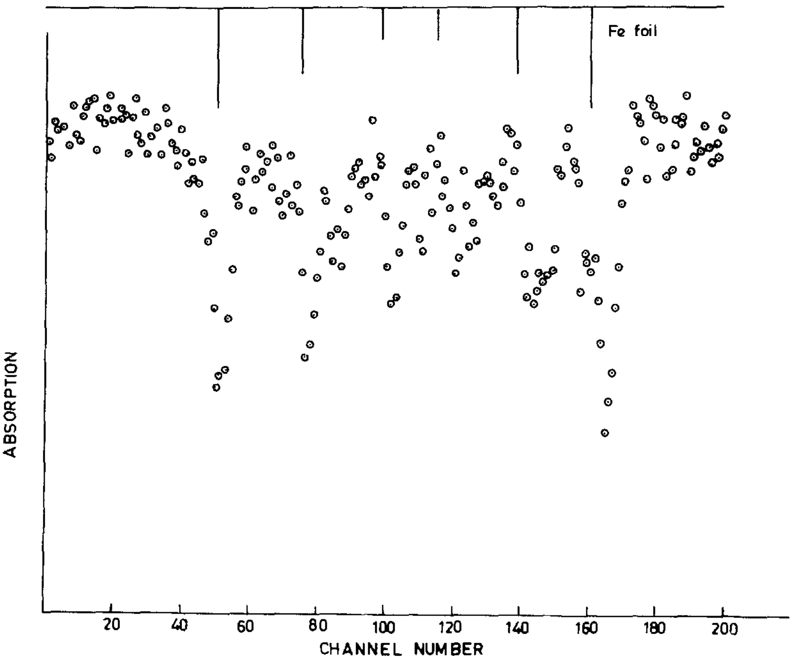

FIG. 4. Mössbauer spectra of Fe_2GaO_4 at 4.6 K.

ence of long-range magnetic order at 4.6 K. At 23.1 K a paramagnetic doublet superimposed on the hyperfine split pattern was observed similar to the finding in the Mössbauer spectra of $FeGa_2O_4$, where the presence of a hyperfine split pattern along with paramagnetic doublet was shown to be due to persistence of short-range ordering in the clusters of Fe^{2+} ions even above the long-range ordering temperature (*1*).

From these results it appears that the anomaly in the magnetization plot of this compound could also be attributed to cluster formation of the Fe^{2+} ions and not due to any noncollinearity of spins. The magnetization plots for $x > 0.2$ do not show any such anomaly indicating that in these compounds there is no clustering of ions.

The magnetization plots for $x > 0.2$ do not show any anomaly and it appears that in these compounds probably there is no cluster formation. Figure 4 shows the spectrum of Fe_2GaO_4 at 4.6 K. The hyperfine pattern clearly indicates the presence of only long-range order in the compound. The Mössbauer patterns of the other compounds have been discussed elsewhere (*6*) and all the patterns below the ordering temperatures show the presence of only long-range order in these compounds.

From all these results it may be concluded that when more than 0.2 mole of Fe^{3+} ions replace Ga^{3+} ions in $FeGa_2O_4$, i.e., more than 0.2 mole of Fe^{2+} is displaced to the octahedral site, the clustering of Fe^{2+} ions is prevented. This is due to an increase in the Fe_B^{2+} concentration brought about by the Fe_A^{3+} ions which displace the Fe_A^{2+} to the B sites. The results also show that with increasing x, the Fe^{3+} ions are distributed between the A and B sites and strong A–B interaction is found in the iron-rich samples.

Acknowledgments

The author thanks Dr. G. C. Hallam and Dr. D. A. Read of the Physics Department of Leeds University, England, for helping with the magnetization and Mössbauer measurements.

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